

Thermochromic Phenomena in Polymers



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Smithers Rapra Update



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1 Introduction

Chromogenic polymers change their visible optical properties in response to an external stimulus [1]. In terms of the specific stimulus they are subclassified as thermochromic (temperature), photochromic (light), electrochromic (electric field), piezochromic (pressure), ionochromic (ion concentration) or biochromic (biochemical reaction). The chromogenic phenomena enable the integration of sensor and actuator functionality or any kind of information respectively into a material itself.

This update is focused on thermochromic phenomena in polymers. Thermochromism can appear in all different classes of polymers: thermoplastics, duroplastics, gels, inks, paints or any type of coatings. The polymer itself, an embedded thermochromic additive or a supermolecular system built by the interaction of the polymer with an incorporated non-thermochromic additive can cause the thermochromic effect. Also, from the physical point of view, the origin of the thermochromic effect can be multifarious. It can come from changes of light reflection, absorption and/or scattering properties with temperature [2].

The content of this review is structured according to the thermochromic material type. Section 2 gives an overview of polymers exhibiting thermochromic properties themselves. Thermochromic polymer systems obtained by doping the polymer matrix with thermochromic additives are reported in Section 3 and Section 4 reviews polymer systems in which the interaction between the polymer matrix and an incorporated additive is the origin of

thermochromism. Finally, in Section 5, polymer systems changing their transparency with temperature by reversible switching between a transparent and a light-scattering state are reviewed. In the literature, this subclass of thermochromic materials is termed thermotropic. At the end of each chapter the state-of-the-art of existing as well as potential future applications based on the specific material classes is discussed. **Table 1.1** displays a listing of the different types of thermochromic polymer materials structured in the first level in the same way as the chapters of this book and in the second level according to the effect of light causing the thermochromism.

Potential applications of thermochromism under development, such as smart windows, tunable light filters, large-area displays as well as sensors that can visualise local surface temperatures, are based on thermochromic polymers. For all these innovations, laboratory prototypes demonstrating the effect have been presented to the public. A very few of them have already reached readiness for marketing and certainly others will follow in the near future.

The literature list gives an actual and representative overview of the field of thermochromic polymers. Patent literature is only cited if it provides a distinctive contribution to the specific topic.

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Table 1.1 Different types of thermochromic polymer material							
Polymers thermochromic themselves		Polymer materials doped with thermochromic additives		Thermochromic through polymer–additives interaction		Thermochromic polymer systems	
Absorption	Reflection	Absorption	Reflection	Absorption	Reflection	Scattering	
	Liquid crystalline polymers with a helical superstructure	Leuco dye-developer-solvent systems			Crystalline colloidal arrays embedded in swollen gel networks	Polymer blends	
Conjugated polymers		Inorganic pigments		Dyes embedded in polymer gel networks		Thermotropic polymer gel networks	
Swollen gel networks of conjugated polymers		Conjugated polymers				Thermotropic casting resin	

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2 Polymers Exhibiting Thermochromic Properties Themselves

2.1 Liquid Crystalline Polymers with a Helical Superstructure

Several liquid crystalline phases – for example nematic and tilted smectic phases – develop a helical superstructure if a chiral dopant is added or the liquid crystalline compound itself has a chiral molecular structure [1, 2]. One enantiomer forms a left-handed and the other a right-handed helical structure with the same pitch (P). The twisted chiral form of the nematic phase is commonly denoted as the cholesteric phase, whereas the twisted chiral forms of all other phases are just marked by an asterisk, e.g., S_C^* for the chiral form of the S_C phase. The helical superstructure is a periodical structure on which incident light satisfying the Bragg condition is reflected. If the wavelength (λ) of the reflected light is in the visible region the liquid crystal becomes intensely coloured. Pitches of the helical superstructure of chiral liquid crystalline phases ranging between about 100 nm and infinite have been observed so far. Besides synthetic compounds, numerous cholesteryl and cellulose derivatives showing in certain temperature ranges selective reflection in the visible region are described in the literature. Generally, the pitch depends on temperature and can be tuned by an external electric field. Thus, these compounds possess thermochromic and also electrochromic properties.

Chiral liquid crystalline polymers with thermochromic properties are also described in numerous publications. Most of them are synthetic polymers. Within the group of biopolymers,

especially, several cellulose derivatives have been found to possess thermotropic and lyotropic cholesteric mesophases with selective reflection in the visible region. One example of a thermotropic liquid crystalline biopolymer is the pentyl ether of hydroxypropyl cellulose [3]. It exhibits a cholesteric phase with selective reflection in the visible region over a temperature range of more than 60 K. Within this temperature range the selective reflection maximum smoothly increases from about 500 nm at room temperature to 650 nm at about 80 °C. By etherification of hydroxypropyl cellulose with a mixture of 99 mol% *n*-pentyliodide and 1 mol% 1,6-diiodohexane a crosslinking of the hydroxypropyl cellulose pentyl ether units with hexyl bridges is achieved. Thereby a polymer network is formed which fixes the helical cholesteric structure [3]. The polymer network obtained is described as a gum of light yellow-green colour. On heating above 100 °C an irreversible unwinding of the helical cholesteric structure occurs and no reflection colour is observed any more even after cooling the sample to room temperature. In tetrahydrofuran, the polymer network was found to swell and to develop a gel structure. Swelling and shrinking of the gel network is accompanied by changes of the cholesteric pitch and thus of the selective reflection wavelength [3]. An example of a biopolymer, which forms lyotropic liquid crystalline phases in binary systems with suitable solvents is hydroxypropyl cellulose. In water as well as in methanol lyotropic cholesteric mesophases with a selective reflection maximum in the visible region are obtained within certain concentration ranges.

The potential application of liquid crystals with helical superstructures in information technology for optical data recording media is one of the driving forces for their material development. This application requires a fixing of the cholesteric order at any user-defined colour [4]. Two methods are used to achieve a fixing of the helical superstructure: to freeze in the

molecular structure by cooling into a glassy state [5-7] or to carry out a crosslinking reaction whereby a polymeric network structure is formed [3, 8–12]. Liquid crystalline polymers exhibiting a glass transition within the cholesteric phase range were successfully used to fix specified colours [5–7]. Within the cholesteric phase range the materials are thermochromic. Depending on temperature, different colours appear which on fast cooling into the glassy state are fixed. However, with these materials the creation of patterns with different colours is difficult since several hours are needed after the temperature changes within the cholesteric phase range until the helical structure reaches an equilibrated state. The preparation of patterned multicolour cholesteric liquid crystal polymer networks by photopolymerisation of a cholesteric mixture has been reported [12]. The polymerisable cholesteric mixture contains only monomers and thus the helical structure has reached an equilibrated state already after seconds. In detail the mixture consist of 20% of a chiral monoacrylate CBC, 25% of a non-reactive commercial chiral dopant CB15 (Merck), 54% of a non-reactive commercial liquid crystal BL59 (Merck), 0.5% of a diacrylate C6M and 0.5% Irgacure 651 photoinitiator. The selective reflection wavelength of the cholesteric phase of this mixture depends strongly on temperature: at 55 °C red light, at 35 °C green light and at 30 °C blue light is reflected. By carrying out the photopolymerisation at different temperatures the respective structure is fixed and red, green or blue polymer networks with a temperature-independent selective reflection wavelength are obtained. In order to prepare a patterned multicolour polymer network masks were used to perform the photopolymerisation step by step in different regions. At each step the temperature and thus the colour of the resulting local polymer network can be chosen. It was concluded that improved local heating and ultraviolet (UV)-induced photopolymerisation techniques enable the production of even more complicated patterned multicolour structures.

2.2 Conjugated Polymers

The occurrence of thermochromic properties is frequently observed in conjugated polymers [13, 14] like polyacetylenes [15], polydiacetylenes [15], polythiophenes [16, 17] and polyanilines [18]. Many conjugated polymers exhibit absorption of light in the visible range as well as a high reflectivity. Hence, they often are coloured and show a metallic appearance. Thermochromism in conjugated polymers has its origin in conformational changes of the polymer backbone, which can occur continuously with temperature or abruptly at phase transitions. Even the slightest modification of the conformational structure can cause significant colour changes. In particular, the planarity of the polymer backbone plays an important role. Any twisting of the chain leads to a decrease of the effective conjugation length and thus to a blue (hypsochromic) shift of the absorption in the UV–visible region. In general the colour changes of conjugated polymers are reversible. However, kinetic effects can cause an irreversibility, which can be useful for thermal recording [19]. An example of a group of thermochromic polythiophenes is reported in [17]. Starting from thiophene derivatives substituted in the 3-position with an azobenzene group via spacers of different lengths either homopolymers or copolymers with 3-hexylthiophene were synthesised. The effect of the azobenzene side chain on the thermochromism of the obtained polythiophenes is discussed in detail. In [20] the synthesis and optical properties of a liquid crystalline polydiacetylene are described. At each of its mesogenic phase transitions a thermochromic effect caused by changes of the conformation of the π -electron system of the conjugated polymer was detected. Note that the thermochromic effect is based on changes of the absorption properties and is not caused by Bragg reflection at a periodic structure changing the lattice spacing depending on temperature as is the case for liquid crystalline phases with helical superstructures. Thermochromic

and mesogenic properties of the polydiacetylene investigated are coupled with one another. The structural and optical properties of poly[2',5'-bis(hexadecyloxy)-1,4-phenylene-1,3,4-oxadiazol-2,5-diyl] are reported in [21]. The polymer was found to possess liquid crystalline properties in a wide temperature range. At 120 °C an order–order transition from a smectic H into a smectic A phase takes place. Moreover, thermochromic behaviour was observed within the temperature range 25–140 °C. With increasing temperature the polymer changes continuously its colour from yellow-green at 25 °C to blue at 130 °C. In order to characterise this thermochromic behaviour in more detail UV–visible absorption and fluorescence emission spectra were measured at different temperatures. For both a continuous evolution with temperature was found. In contrast to the results reported in [20] here even at the smectic H to smectic A phase transition no discontinuous change of the UV–visible and fluorescence intensities could be detected. Reversible or irreversible colour changes of conjugated polymers occurring at a phase transition between two solid phases were observed in urethane substituted polydiacethylenes [22]. Depending on the alkyl chain length an even–odd effect for the reversibility of the thermochromic phase transition was found. A chain length of five carbon atoms leads to a reversible transition between the blue A phase and the red B phase, whereas urethane substituted polydiacethylenes with even-numbered chain length 4 and 6 turn to the red B phase on heating but do not completely return to the initial blue A phase even when cooled to room temperature. An even–odd effect was also observed for the thermochromic effect occurring at the rod-to-coil transition of poly(*n*-butoxycarbonylmethylurethane)-diacetylenes (BCMU) [23]. Some BCMU show a blue to yellow and BCMU even a red to yellow colour change. The transition from the rod state at room temperature to the coil state at 65 °C causes not only a thermochromic colour change but also a decrease of the photoconductivity.

Conjugated structures can also be prepared by using different precursor polymers [24]. Such a system is obtained by a combination of two dithiocarbamate polymers and the corresponding conjugated polymers: poly(3,4-diphenyl-2,5-thienylene vinylene) and poly[3,4-bis(4-buthylphenyl)-2,5-thienylene vinylene]. It should be noted that the introduction of the butyl side chain led to high solubility in common organic solvents, a necessary condition for polymer casting processes.

The thermochromic properties of multilayered polydiacetylene vesicles are discussed in [25]. A layer-by-layer structure is obtained by an alternate deposition of positively charged photopolymerised polydiacetylene vesicles and negatively charged linear polymers (polystyrene sulfonate or polyvinyl sulfate). A glass slide is used as carrier for the multilayered polymer system.

Thermochromic effects of conjugated polymers are also observed in Langmuir–Blodgett films. Investigations of mixed Langmuir–Blodgett films of poly(3-hexylthiophene), poly(3-octylthiophene) and poly(3-octadecylthiophene) with arachidic acid have been reported [26]. With increasing temperature the absorption maximum of the undoped films shifts to higher energies. In comparison to spin-coated thin films of the same materials the shift of the absorption peak with temperature occurred in the Langmuir–Blodgett films at lower temperatures. The observed temperature-dependent changes of the optical absorption were only partly reversible.

Thermochromism triggered by conformational changes also occurs in poly(di-*n*-hexylsilane) [27]. The thermochromic transition at about 42 °C involves three structural aspects: first, a disordering of the alkyl side chains but with preferential disposition normal to the main-chain backbone; second, a partial disordering of the backbone conformation; third, a high increase of the intermolecular order, as the polysilane chains are effectively

packed as cylinders in a hexagonal lattice structure. This work is a descriptive example of the interaction between conformational changes and thermochromic properties.

2.3 Swollen Gel Networks

Thermochromic gel networks obtained by the swelling of conjugated polymers in gel-forming organic solvents are frequently reported [28, 29]. The origin of the thermochromic effect of these gels is a change of the molecular structure of the polymer backbone occurring at the gel–sol (gel to solution) transition. Gels consisting of polydiacetylene and *o*-dichlorobenzene or other gel-forming systems are presented in [28]. At the respective gel–sol transition temperatures reversible pronounced colour changes are observed. Colours and transition temperatures are found to depend on the specific gel-forming solvent used as well as on the proportion between polymer and solvent. Another example is reported in [29]. A gel formed by poly[2-(3,7-dimethyloctoxy)-5-methoxy-1,4-phenylenevinylene] in benzene shows a gradual red to yellow colour change on heating at about 35 °C. At this temperature a gel–sol transition takes place. In the absorption spectrum of the gel phase a peak with a distinct shoulder appears in the visible region. On heating from the gel into the solution state the shoulder disappears. The yellow sol state of the mixture remains metastable on cooling from above the sol–gel transition temperature back to room temperature. Eventually after several hours the mixture reverts to the red gel phase. The thermochromic effect is explained by a reduction of interchain π – π interaction during the transition from the gel state into the solution state. Whereas in solution only isolated polymer chains are present, the structure of the gel state consists of aggregated and isolated chain sections.

A reversible thermochromic effect is also observed in polymer gel films based on a polyphenylenevinylene polymer [30]. The

preparation was carried out by dissolving the polymer and the plasticiser dibutyl sebacate in a suitable solvent followed by spin casting and finally drying under vacuum (1.3×10^{-4} Pa). On heating from 25 to 100 °C a reversible continuous colour change from red to yellow occurs in the obtained polymer gel films. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels were found to depend on temperature. Both levels shift at different rates resulting in an overall increasing band gap energy with increasing temperature. No volume change or phase change of the polymer gel film was visually observed within this temperature range. The authors discuss that on heating the film, which is at room temperature rather solid, it transforms into a more gel-like state. However, an additional plasticiser is required to support the effect. Without plasticiser the effect appears to be slower, slightly less reversible and less dramatic.

2.4 Applications

Because of the poor stability of thermochromic liquid crystals in the neat form, commercial products are usually based on microcapsules containing the liquid crystals and protecting them against the matrix materials. The majority of thermochromic liquid crystal-containing commercial temperature-indicating devices consist of three layers: a protective clear polyester substrate layer, a printed ink layer containing a microencapsulated cholesteric liquid crystal and a printed black backing layer. The temperature indicators can detect temperature changes ranging from a fraction of a degree to over 20 °C by varying their colour continuously through the entire visible region.

The advantage of liquid crystalline-based thermoindicators is the possibility to detect temperature changes even smaller than 1 K. Disadvantages are their relatively high costs and their limited

processing stability. For example, use of these thermochromic liquid crystalline-based thermoindicators in extrusion processes is not possible.

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3

Polymer Materials Doped with Thermochromic Additives

Another way to obtain thermochromic polymers is to incorporate a thermochromic material into a polymer matrix. Both components build separate phases and do not influence the phase structure of the other component. Microencapsulated leuco dye–developer–solvent systems, inorganic pigments and conjugated polymers are suitable candidates for this purpose. Leuco dye–developer complexes are by far the most important systems to achieve thermochromic properties for different polymer materials by realising a separate phase of the thermochromic system in a non-thermochromic polymer matrix. With regard to their importance for the development of thermochromic materials the properties of these complexes are discussed in much more detail than those of inorganic thermochromic pigments or thermochromic conjugated polymers.

3.1 Leuco Dye–Developer–Solvent Systems

Leuco dye–developer–solvent systems consist of an electron-donating chromogenic compound (leuco dye), an electron acceptor (developer) and a matrix component (solvent) [1]. The most common electron-donating chromogenic compounds are phenylmethane and fluoran derivatives bearing a lactone ring moiety. In the lactone ring-closed state these so-called leuco dyes or colour formers [2] are either colourless or weakly yellow coloured. On reaction with an electron-accepting developer an opening of the lactone ring occurs resulting in the formation of a

zwitterionic structure. As a result of this reaction the conjugated π -electron system of the dye is extended and the longest wavelength absorption peak shifts from the UV to the visible range. Thus the dye becomes coloured. The addition of an appropriate solvent component enables the colour-forming reaction to be reversible with temperature. Leuco dye–developer–solvent systems are coloured in the solid state and transform on heating above their melting temperature into a colourless liquid. In the molten state the solvent functions as an inhibitor of the colour-forming reaction, whereas it obviously does not interfere with the colour formation in the solid state. An example of a reversible thermochromic leuco dye–developer–solvent system is a mixture of 1 wt% 2-chloro-6-diethylamino-3-methylfluoran, 5 wt% 2,2'-bis(4-hydroxyphenyl)propane and 94 wt% 1-hexadecanol. On cooling below 48 °C the colourless molten state develops a vermillion colour when crystallisation takes place.

Although the colour-forming reaction of leuco dyes has been known for more than 50 years, the detailed molecular mechanism of this reaction is still unclear. Until about 15 years ago a proton-triggered ring-opening/ring-closing mechanism was the only model discussed in the literature. According to this model the acidity of the developer is a measure for its effectiveness to drive the ring-opening/ring-closing equilibrium of leuco dyes towards their ring-open coloured state. In many cases, this simple model fails to explain the experimental results [3]. Investigations on the binary system of the leuco dye crystal violet lactone (CVL) and the developer bisphenol A (BPA) first revealed that leuco dye–developer complexes are formed in the coloured solid state [4]. The Job method was used to determine the leuco dye–developer ratio in the complexes. One CVL molecule was found to be associated with four BPA molecules. This experimental result is in accordance with the prediction of MM-2 calculations on the same system [5]. The formation of leuco dye–developer

complexes in the coloured solid state was also reported in [6]. The authors of that study investigated a binary system of the same leuco dye CVL in combination with the developer lauryl gallate (LG) and observed the formation of coloured complexes with an equilibrium stoichiometry of $(LG)_3CVL$ after cooling from the melt. Infrared (IR) and Raman spectra show that hydrogen bonding between the carboxylate group of the ring-open CVL and the protons from LG increases in the system as the complex is formed. This leads to a stabilisation of the zwitterionic ring-open state of the CVL molecule. A third example of the formation of leuco dye–developer complexes is reported in [7]. The system investigated is composed of the fluoran leuco dye 2'-anilino-6'-(N-ethyl-N-isopentyl)amino-3'-methylspiro[isobenzofuran-1(3H),9'-(9H)xanthen]-3-one (S-205) and the developer BPA. A leuco dye–developer complex with a definite molar ratio of S-205:BPA = 1:4 was isolated and spectroscopically analysed by IR and nuclear magnetic resonance. Hydrogen bonding was also pointed out in that paper [7] to be the principal factor for the formation of the coloured complexes. Investigations on the molecular structure of three leuco dye–developer complexes using X-ray crystallography have been reported [8]. Each complex consist of the leuco dye rhodamine B base in combination with one of the following three phenols: ethyl gallate, 3,4-dihydroxybenzoic acid ethyl ester or 4-hydroxybenzophenone. For all three complexes only an equimolar ratio of the complex partners was found in the molecular structures of the isolated coloured species. Although two references [4, 6] are cited, no discussion about the different leuco dye–developer ratios obtained in the coloured complexes is made. The authors found that for the investigated developers with two or three hydroxyl groups, hydrogen bonding via two OH groups occurs and they concluded that this stabilises the entire complex by electron delocalisation.

Reversible thermochromic systems generally consist of at least three components: a leuco dye, a developer and a solvent component.

The additional third component makes the systems even more complex. Most of the solvent components described in the literature consist of a long hydrocarbon chain bearing a polar end group on one side of the chain. Some examples are 1-alcanols, 1-alcylamides and 1-alcanoic acids with chain length of more than six carbon atoms. This structure allows a disperse–disperse interaction via the hydrocarbon chain and polar–polar interaction via the polar end group. In leuco dye–developer–solvent systems, especially polar–polar interaction between the solvent and the developer can occur. The reversible thermochromic effect of these systems is explained by a competition between dye–developer and solvent–developer interactions [9, 10]. In the solid state the dye–developer interactions prevail and coloured dye–developer complexes are formed. On heating from the solid into the molten state solvent–developer interactions become dominant. The dye–developer complexes are destroyed and decolourisation of the systems takes place. Indeed investigations of binary phase diagrams of certain developer–solvent systems give evidence for the formation of developer–solvent complexes with fixed stoichiometric ratios. Congruently melting compounds composed of two developer molecules and one solvent molecule are observed in the binary phase diagrams between various alkyl gallates (developer) and 1-alcanols (solvent) [9, 11]. Another example is the formation of 1:1 proton transfer complexes between phenols and amines [12].

Although there are numerous examples of reversible thermochromic leuco dye–developer–solvent systems, very few examples of reversible thermochromic two-component systems have been reported, in which one component combines the function of solvent and developer [13–15]. In contrast to the three-component leuco dye–developer–solvent systems, the reversible thermochromic two-component systems are colourless in the solid state and coloured in the molten state. One example of these systems is a 1:7 mixture of the fluoran leuco dye 2'-(*o*-chloroanilino)-6'-di-

n-butylaminospiro[isobenzofuran-1(3*H*),9'-[9*H*]xanthene]-3-one with octadecylphosphonic acid. On heating above 100 °C the mixture completely melts and becomes coloured. Cooling at low rates results in a crystallisation of the mixture at about 70 °C accompanied by a decolorisation, whereas fast quenching maintains the coloured state. Similar behaviour was also observed for other thermochromic two-component mixtures.

Thermochromism in hydrogen bonding-based phenol–amine complexes dissolved in non-polar solvents is also known [12]. Note that typical developer and solvent components are present in this system, but no leuco dye. The thermochromic behaviour was found to depend particularly on the stoichiometric ratio between the amine and the phenol. A solution of 3,3'-dibromo-5,5'-dinitro-2,2'-biphenyldiol and diisopropylamine with a molecular ratio of 1:1 showed no thermochromism, while solutions with ratios of 1:2 or higher showed thermochromism. This result is explained by assuming that the proton-transferred species are 1:2 complexes. The authors conclude that the proton-transferred complexes are formed in polar solvents at low temperature if an appropriate hydrogen bonding network between phenol and amine molecules can stabilise them.

Such experiments confirm the complexity of thermochromism in multicomponent systems. Even a combination of the ring-opening/ring-closing mechanism of leuco dyes with proton-transferred complexes or the formation of helical liquid crystalline superstructures should be in general possible.

3.1.1 Thermochromic Thermoplastic Polymers

Thermochromic thermoplastic polymers based on leuco dye–developer–solvent systems have been described in the literature [16–19]. Polyethylene was the first choice for the polymer matrix.

By adding both the developer BPA and the leuco dye CVL, a polyethylene material which is blue in the solid state and colourless in the molten state was obtained. Similar behaviour was observed if polyethylene was substituted by polypropylene. Moreover, the effect of the addition of a low molecular mass solvent component exhibiting a lower melting temperature than the polymer matrix is reported. On adding small amounts of the low molecular mass solvent component a two-step switching process takes place in the resulting polymer system. At the melting temperature of the low molecular mass solvent component a decrease of the colour intensity and finally at the melting temperature of the polymer system a transformation into a colourless liquid state occur. A further increase of the amount of the added low molecular mass solvent component leads to an increasingly pronounced colour intensity change at the melting temperature. If the added monomeric solvent component has a much stronger affinity for the developer and leuco dye than the polymer matrix, the concentration of the colour-forming components in the polymer matrix becomes very small. To achieve such a high affinity the addition of surface-active compounds is necessary. Thus the polymer phase becomes colourless in solid and liquid states and only at the melting temperature of the monomeric solvent component does thermochromic switching occur.

Examples of thermochromic polyethylenes and polypropylenes of this type have been reported [16, 17]. The findings show that thermochromic composites are convenient additives for polyolefins and that the resulting thermochromic polyolefin materials are extrusion stable. Thermochromic polyolefin flat foils with a thickness of approximately 100 μm were investigated. They were manufactured by extrusion technology at extrusion temperatures of 150 °C (polyethylene) or 230 °C (polypropylene) and slot die temperatures of 170 °C (polyethylene) or 240 °C (polypropylene). The stability of the thermochromic polymer materials in the extrusion process demonstrates their excellent thermal and

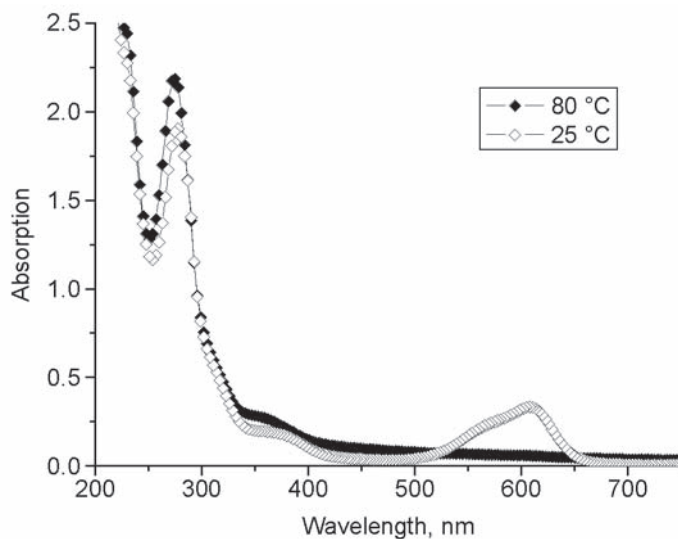


Figure 3.1 Absorption spectra of a 100 μm thick polyethylene flat foil comprising 5 wt% of a thermochromic composite at 25 and 80 $^{\circ}\text{C}$

mechanical stability. The optical properties of the thermochromic polyolefin foils obtained were characterised by UV–visible spectroscopy. Both forms of the leuco dye, the ring-open coloured form (absorption in the visible region) and the ring-closed leuco form (absorption in the UV region), were detected. As an example, **Figure 3.1** displays the absorption spectra of a thermochromic polyethylene foil at two temperatures (25 and 80 $^{\circ}\text{C}$).

At 25 $^{\circ}\text{C}$ the foil is in the coloured state as can be seen by the appearance of an absorption peak in the visible region ($\lambda_{\text{max}} = 608 \text{ nm}$). In the spectrum measured at 80 $^{\circ}\text{C}$ this absorption peak has completely disappeared. Simultaneously an increase of the absorption peak in the UV region ($\lambda_{\text{max}} = 276 \text{ nm}$) takes place.

This behaviour is in accordance with the model of a temperature-dependent reversible equilibrium between the ring-open and ring-closed state of the leuco dye as the origin of the thermochromic effect. The leuco dye used in this polymer foil is CVL. The absorption peak at $\lambda_{\text{max}} = 276 \text{ nm}$ corresponds to the ring-closed colourless leuco form and the absorption peak at $\lambda_{\text{max}} = 608 \text{ nm}$ to the ring-opened blue zwitterionic form of CVL. It was concluded that the thermochromic switching mechanism in these thermochromic polymer materials is the same as in low molecular mass leuco dye–developer–solvent systems. As a further result, no changes in the temperature-dependent absorption spectra were observed if the polyethylene matrix was exchanged for polypropylene without any changes of the thermochromic composite. Investigations on the concentration dependence of the thermochromic composite (leuco dye, developer and monomeric solvent) on the colour intensity of the obtained polyolefin foils revealed a direct proportionality between the composite concentration and the resulting colour intensity in accordance with Beer's law (**Figure 3.2**).

Thus the adjustment of the colour intensity is quite simple. This result indicates that the interactions of the different components of the thermochromic composite with one another dominate against their interactions with the polymer matrix. Neither dye aggregate phenomena nor the formation of novel structures induced by polymer–composite interaction occur within the investigated concentration range. The influence of the structure of the developer on the colour intensity of the obtained thermochromic polyolefin foils was investigated in [18]. Two series of polypropylene flat foils comprising 10 wt% of a leuco dye–developer–solvent system with a molar ratio of 1:3:45 were prepared by extrusion technology under the same processing parameters. The solvent component was kept unchanged. In series 1 the leuco dye RED-40 and in series 2 the leuco dye CVL was used. The structures of these two leuco dyes are displayed in **Figure 3.3**. Both dyes have a phthalide structure.

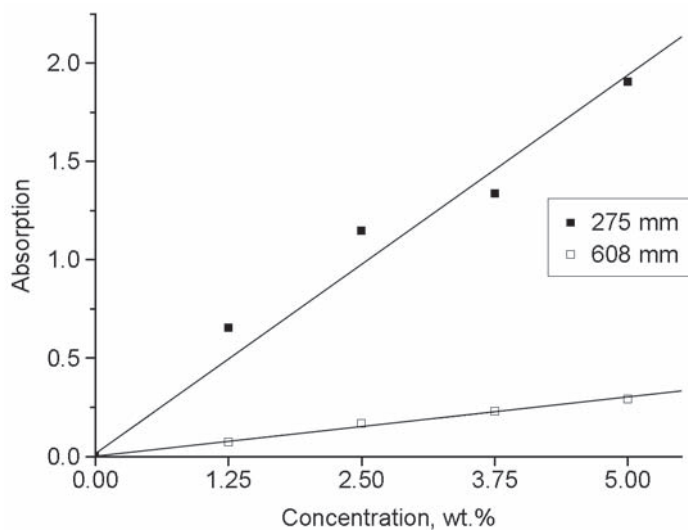


Figure 3.2 Intensity of the absorption maxima at 275 and 608 nm of polypropylene flat foils as a function of the concentration of the incorporated thermochromic composite

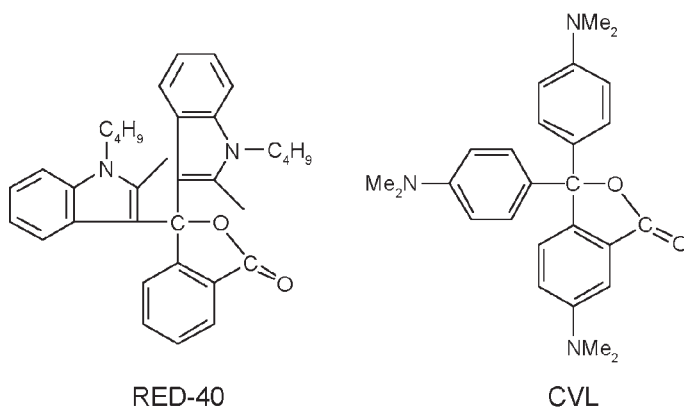


Figure 3.3 Structures of the leuco dyes investigated

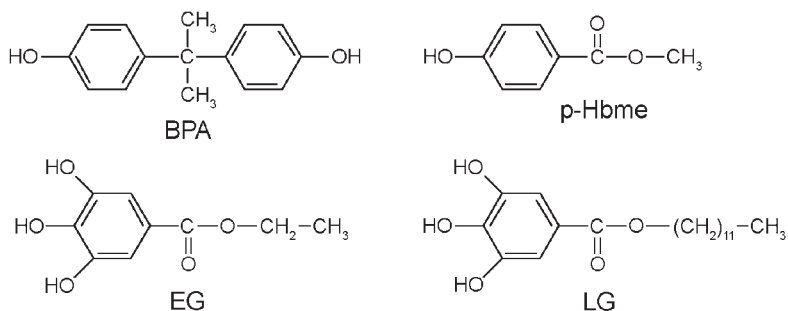


Figure 3.4 Structures of the developers investigated

Within each series the developer was varied. The structures of the four developers investigated are displayed in **Figure 3.4**.

All the developers were phenols with one or three phenolic OH groups on one side and either a long non-polar hydrocarbon chain or a short polar group on the other side of the molecule. The UV-visible spectra of the thermochromic polypropylene flat foils of both series, measured at room temperature, which is far below the switching temperature, are shown in **Figure 3.5**.

The results show two effects. First, that the ranking of the four developers in both series is different. Whereas in series 1 the highest colour intensity is obtained by using the developer BPA, in series 2 EG develops best. This result is explained by expecting the formation of dye-developer complexes with different stoichiometric ratios. The second effect is that the gallate developer bearing a long non-polar hydrocarbon chains on the other side of the molecule (LG) leads to much lower colour intensities than the shorter homologous EG. This effect is explained by comparable stronger interactions of these developers with the non-polar solvent matrix. An influence of further additives on the resulting colour intensity was demonstrated by adding a long-chain alkanol to two thermochromic polypropylene

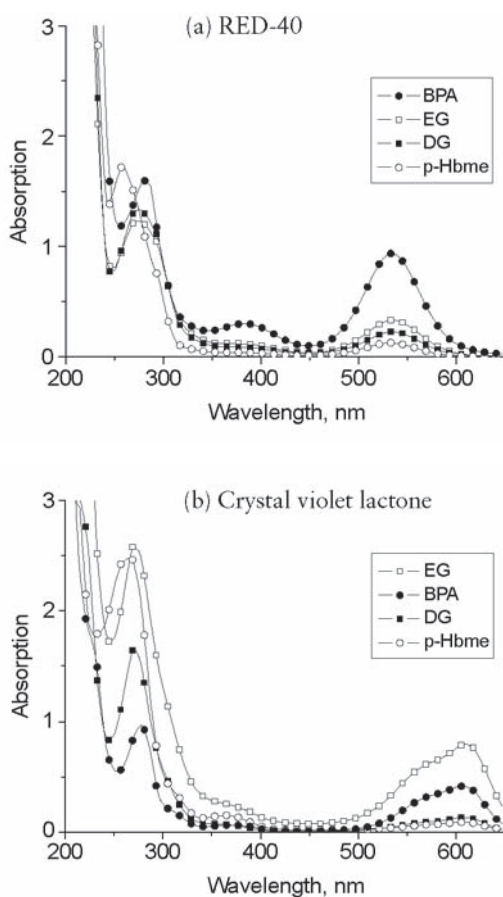


Figure 3.5 Transmission spectra of two series of 100 μm thick polypropylene flat foils comprising 10 wt% of a leuco dye-developer-solvent system measured at 25 $^{\circ}\text{C}$: (a) RED-40 leuco dye (series 1); (b) CVL leuco dye (series 2)

foils comprising either LG or EG as developer. LG can interact with the added alcohol in two ways: by disperse–disperse interaction via the long hydrocarbon chain or by polar–polar interaction via the phenol groups. EG enables only polar–polar interactions with the added alcanol. As a consequence of this the addition of the alcanol was expected to interfere with leuco dye–developer complex formation more in the case of EG than in the case of LG. Indeed this effect was experimentally observed.

The preparation of thermochromic thermoplastic materials by extrusion technology is also described in [20]. One example is a formulation of 1.4 g (0.2 wt%) of 2,3-bis(dodecylsulfonyl)-6,11-dihydroxy-naphthacene-5,12 dione, 21 g (3 wt%) poly [[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl] [(2,2,6,6-tetramethyl-4-piperindinyl)imino]-1,6-hexanediyl [(2,2,6,6-tetramethyl-4-piperindinyl)imino]] (base 1; Chimassorb® 944) and 677.6 g (96.8 wt%) polypropylene powder (Moplen HP 500H – melt index 1.8 (230 °C/2.16 kg) – purchased from Basell). The formulation was mixed in a turbo mixer and afterwards extruded at 190–230 °C to give polymer granules which were subsequently converted into plaques (1 mm thick) using a press-moulding machine operating at a maximum temperature of 240 °C and a pressure of 20 000 lb. A series of other analogue formulations just differ in the mixing ratio or use derivatives of the dye and base starting components. The thermochromic polypropylene materials obtained are blue or violet in colour at room temperature. On heating above 100 °C the colour changes to red. Calorimetric measurements are mentioned to show how efficiently the colour of the plaques changes with temperature. Spectroscopic investigations of the interdependency between colour and temperature were not carried out. Besides polypropylene, the reversible thermochromic composition can comprise plastic articles, films, papers, fibres, solvents, waxes, coatings or inks as carrier materials. However, no example of any final polymer product with reversible thermochromic properties is reported.

As a particular case of thermoplastic polymers, fibre materials should be mentioned. Thermochromic cellulose fibres, which were fabricated by incorporating the commercial thermochromic pigment Chromicolor® AQ-INK, magenta type#27 (Mitsui International Co.) are described in [21]. This thermochromic pigment is a microencapsulated reversible switching leuco dye–developer–solvent system. The diameters of the microcapsules range from 0.5 to 5 μm . The fabrication of the thermochromic cellulose fibres has been carried out by dispersing the thermochromic pigments homogeneously into a cellulose spinning solution followed by spinning fibres from the modified solution. The fibres obtained are reported to exhibit a thermochromic colour intensity change from magenta to colourless at a temperature of 32.7 to 32.9 °C. It should be mentioned that a switching range of 0.2 K is a surprising result. Usually, the switching of leuco dye–developer–solvent systems requires a temperature range of at least 1–2 K. Such a small temperature range as reported for the thermochromic cellulose fibres could only be realised by using thermochromic liquid crystals instead of leuco dye–developer–solvent systems. Furthermore, differential scanning calorimetry (DSC) measurements of the fibres are reported, showing that the melting process which triggers the thermochromic switching of the Chromicolor® pigments still occurs in the thermochromic cellulose fibres. However, no direct measurements of the thermochromic effect are presented. Note that DSC measurements can detect the melting process, but cannot verify that the composition of the leuco dye–developer–solvent system is unaffected by the polymer processing procedure and that the thermochromic colour intensity change still occurs in the polymer matrix.

3.1.2 Thermochromic Thermosetting Polymers

Once the polymer network of thermosetting polymers has been built up a dispersion of additives in the polymer is no longer possible. To dope thermosetting polymers, the additives must be added to the

highly reactive monomers before the crosslinking reaction is carried out. Incorporation of a thermochromic leuco dye–developer–solvent system into a matrix comprising a component which reacts with at least one of the components of the composite requires separation of matrix and composite from each other. In [19] two different microencapsulation processes are described which are both suitable to encapsulate thermochromic composites and thus to build up a protective shield with low porosity. One microencapsulation process produces a melamine resin and the other an epoxy resin shell around the thermochromic composite core material. Whereas encapsulation with melamine resin is a common method widely described in the literature [22, 23], only a few examples of encapsulation with epoxy resin have been reported so far [24].

The first step of both these microencapsulation processes is to emulsify the respective thermochromic leuco dye–developer–solvent system in an aqueous solution. This process determines the size and size distribution of the final microcapsules obtained. An emulsion of thermochromic composites in water was achieved by the addition of a surface-active compound. Since surface-active compounds can interfere with the formation of complex between leuco dye and developer and also the interface polymerisation reaction of the microencapsulation process, extensive work has been done to select system-compatible surface-active compounds. An anionic (3-(*N,N*-dimethyldodecylammonio)-propanesulfonate), a zwitterionic (dodecylsulfobetain), a cationic (*N*-cetyl-*N,N,N*-trimethylammonium bromide, CTAB), a non-ionic (Tergitol® NP-9) and a polymeric surfactant (polyvinyl alcohol) were tested. For the microencapsulation of a thermochromic composite consisting of 1-octadecanol, BPA and CVL, the zwitterionic and the cationic surfactant were found to give the best results. However, the different influences of the surfactants could not be explained.

The subsequent shell formation was carried out by an interface polymerisation reaction. In one of the two reported processes

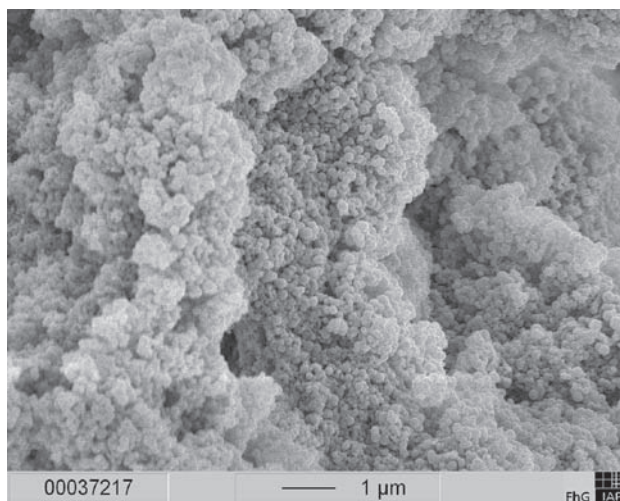


Figure 3.6 Melamine resin-encapsulated thermochromic composite

encapsulation with melamine resin was conducted. A cotensid guiding the polymerisation reaction to the water–organic interface was used in combination with a surface-active compound for the emulsification of the thermochromic composite. After the emulsification was completed a methylol melamine precondensate was added to start the interface polymerisation reaction. The resulting microcapsules were isolated by filtration. Capsules with a narrow size distribution and average size of typically a few micrometres were obtained by this method. In exceptional cases sizes below 1 μm were obtained (see **Figure 3.6**).

The second process reported was an epoxy resin encapsulation process. This process requires no cotensid. However, the high reactivity of both resin and crosslinking hardener must be considered during all steps of the preparation. Competing side reactions between the thermochromic composite and the shell

building components need to be minimised. This was achieved by creating a layer-by-layer reaction at the interface. A water-insoluble epoxide was dissolved in the molten thermochromic composite prior to the emulsification and the interface polymerisation reaction was started after the emulsification by adding the water-soluble triamide: diethylene triamine (DETA). Since one of the components which react with the epoxy resin is located in the organic phase and the other in the aqueous phase their reaction occurs at the interface. The size of the microcapsules obtained typically varies between 2 and 20 μm . As an example, **Figure 3.7** shows a raster electron microscopy (REM) image of one of the prepared epoxy resin-encapsulated thermochromic composites. A mixture of microcapsules with a round geometry, deformed microcapsules and crystals of non-encapsulated thermochromic composite can be seen. Cluster formation of the capsules does not take place.

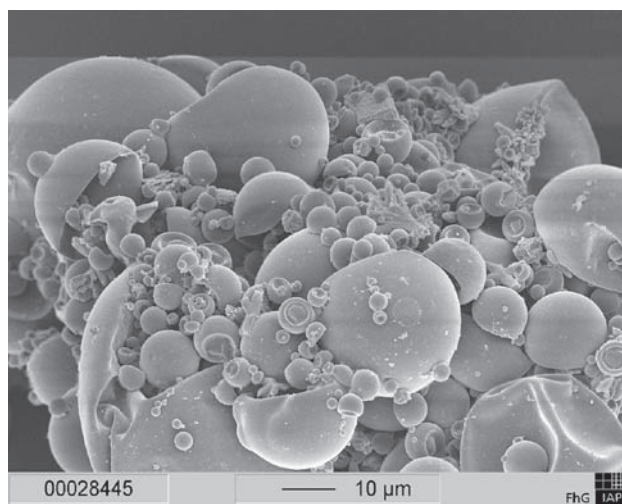


Figure 3.7 Epoxy resin-encapsulated thermochromic composite

With both methods, microcapsules with core-shell geometry were obtained. The advantage of the melamine resin capsules is that porosity and elasticity of the shell can be adjusted within wide ranges by controlling the degree of crosslinking. In comparison to the epoxy resin microcapsules smaller sizes and narrow size distributions were obtained. The advantage of epoxy resin capsules is the much higher transparency of the shell and the better temperature stability in comparison with melamine resins.

In most potential future applications of thermochromic materials the temperature-displaying colour change is intended as an additional functionality. Well-established materials for specific applications have to be modified so that they become thermochromic. An ideal thermochromic additive induces thermochromism without altering any other material properties. Especially, the mechanical characteristics of materials are important criteria in many applications. Concentration, size, size distribution, cluster formation and the interface forces of an incorporated additive have an effect on how strong the matrix properties are influenced. Although mechanical properties are an important factor for the commercialisation of thermochromic materials, mechanical measurements to elucidate the influence of the addition of thermochromic microcapsules on the resulting mechanical properties of the matrix are only rarely reported.

In [19] E-modulus and bending strength of epoxy resin samples with and without doping of different thermochromic melamine resin microcapsules ($c = 4$ wt%) are reported. The results of these measurements are shown in **Figure 3.8**.

The melamine resin microcapsules used contain thermochromic leuco dye-developer-solvent systems as core materials which switch from blue (sample 1), red (sample 2) or green (sample 3) to colourless at 60 °C. Their size ranges are 1–3 μm (sample 1), 0.5–4 μm (sample 2) and 5–10 μm (sample 3). As can be seen in

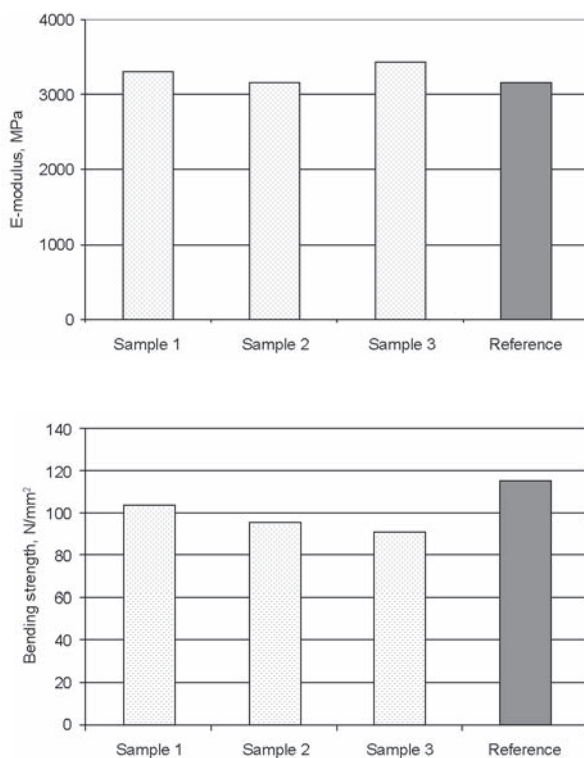


Figure 3.8 E-modulus and bending strength of an epoxy resin reference sample and of three epoxy resin samples modified by the addition of 4 wt% of thermochromic melamine resin microcapsules

Figure 3.8, a slight increase of the E-modulus and a small reduction of the bending strength of the polymer material occur due to the addition of the thermochromic microcapsules. The increasing reduction of the bending strength from about 6% for sample 1 to about 15% for sample 3 is attributed to the rising particle size. It was concluded that a reduction of the observed drop of the bending strength should be possible by reducing the particle size of the thermochromic microcapsules. This conclusion was supported by an REM image presented of the surface of a fractured epoxy resin sample containing 4 wt% of a microencapsulated thermochromic composite. Positions where microcapsules are located are distinctly visualised in the REM image.

3.1.3 Light Stability of Leuco Dyes

The light stability of leuco dyes is rather poor. Fading of the coloured zwitterionic ring-open form occurs on exposure to UV light as well as visible light. The photostability is found to be particularly sensitive to environmental factors, such as the substrate and the presence of oxygen and water. Analysis of intermediates and final products of the photodecomposition of leuco dyes suggests three possible pathways: dealkylation of the alkylamino groups via the formation of an N-oxide, oxidative cleavage by a reaction with singlet oxygen or reduction of the excited dye cation state to a colourless leuco form [25]. The contribution of these different pathways to the overall photo-fading process occurring depends on the experimental conditions as well as on the specific leuco dye-developer system and its environment. Investigations of the effect of stabilisers on the photo-fading process of leuco dyes have led to the discovery of particular leuco dye-matrix-stabiliser systems in which the photo-fading process of the leuco dye is almost completely inhibited [26–28]. However, none of these leuco dye-matrix-stabiliser systems possesses reversible thermochromic properties.

3.2 Inorganic Pigments

In contrast to the thermochromic effect of organic composites, thermochromism of inorganic materials, such as metal salts and metal oxides, has been well known for a long time [29–31]. The appearance of thermochromism in inorganic pigments has its origin in changes of crystal structure. For example, the red to brown colour change of copper mercury iodide, $\text{Cu}_2(\text{HgI}_4)$, is caused by a change from an ordered to a disordered structure. In both modifications the iodide ions form a face-centred cubic cell with tetrahedral holes which are partly occupied by the copper and mercury ions. In the low-temperature modification definite tetrahedral holes are occupied, whereas in the high-temperature modification the cations are randomly distributed throughout all of the tetrahedral holes. Another example is mercury(II) iodide. The transition from the α - to the β -modification at 127 °C is accompanied by a colour change from red to yellow. Colour changes and respective transition temperatures of several inorganic pigments are listed in **Table 3.1** In most of the inorganic pigments considered the thermochromic effect appears at temperatures above 100 °C and is irreversible. Only the last three examples listed in **Table 3.1** exhibit reversible thermochromic behaviour.

An unprecedented one-finger-push-induced phase transition with a drastic colour change in an inorganic material is discussed in [32]. The colour transition in the $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ system from green to brownish-red occurs during a first-order phase transition. This study shows that it is possible to control this transition in terms of temperature or pressure with respect to the tungsten content. It is noted that the initial colour is reversed upon annealing. Therefore, such metal complexes combine thermochromism and piezochromism in one material and could be called chromogenes.

Table 3.1 Thermochromic inorganic pigments with reversible (\leftrightarrow) or irreversible (\rightarrow) colour changes		
Inorganic pigments	Colour change	Temperature (°C)
$\text{Ni}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$	light green \rightarrow grey	~120
$\text{Cu}(\text{CNS})_2 \cdot 2\text{-pyridine}$	green \rightarrow yellow	~135
	yellow \rightarrow black	~220
$(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$	yellow \rightarrow black	140–160
$\text{Co}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$	fuchsia \rightarrow deep blue	~140
	deep blue \rightarrow grey	~500
NH_4VO_3	white \rightarrow brown	~150
	brown \rightarrow black	~170
$[\text{Co}(\text{NH}_3)_6]\text{PO}_4$	yellow \rightarrow blue	~200
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	yellow \rightarrow grey	~200
$[\text{Co}(\text{NH}_3)_6](\text{C}_2\text{O}_4)_3$	yellow \rightarrow violet	~215
	violet \rightarrow brown	250–270
	brown \rightarrow black	320–350
$\text{Mn}(\text{NH}_4)\text{P}_2\text{O}_7$	violet \rightarrow white	~400
$\text{Cu}_2(\text{HgI}_4)$	red \leftrightarrow brown	~70
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMTA} \cdot 10\text{H}_2\text{O}$	pink \leftrightarrow purple	~75
HgI_2	red \leftrightarrow yellow	~127

3.3 Conjugated Polymers

The use of poly(3-alkyl thiophene)s as thermochromic pigments for the introduction of thermochromism into host polymers has been reported [33, 34]. Poly(3-alkyl thiophene)s belong to the group of conjugated polymers exhibiting thermochromism due to temperature-dependent conformational changes of the conjugated π -electron system. To vary the switching temperature of the polythiophene pigments, modifications of their chemical structure are necessary. A set of poly(3-alkyl thiophene)s that visually and reversibly change colour at a prescribed temperature in the region of -35 to $+125$ °C were developed. However, no list of chemical structures and corresponding switching temperatures of the investigated polythiophene pigments was published. The pigments obtained were reported to be thermally stable to above 200 °C. By dispersing 0.1 – 1.0 wt% of them into commercially available paints, plastics and rubbers visible thermochromic effects were observed in the doped host polymer matrices.

3.4 Comparison Between the Three Different Classes of Thermochromic Additives

A comparison between the classes of thermochromic additives presented in Sections 3.1–3.3 is given in **Table 3.2**. The outstanding property of organic thermochromic materials is that switching temperature and colour can be customised. Moreover, the narrow absorption band allows the creation of multiple switching effects by a combined use of several thermochromic additives. With a view to application, these properties are very important. They enable a flexible adjustment of the thermochromic properties for specific application. The advantage of inorganic pigments is their thermostability above 200 °C and their light stability which is even suitable for outdoor application. However, most of the inorganic pigments for these applications are toxic.

Table 3.2 Comparison between thermochromic inorganic pigments, organic thermochromic microcapsules and conjugated polymers			
Material property	Inorganic pigments	Organic microcapsules	Conjugated polymers
Switching temperature	70–500 °C	0–130 °C	?
Thermostability	Stability at 500 °C possible	<200 °C	<200 °C
Light stability	Suitable for outdoor applications	Insufficient	Insufficient
Multiswitching between different colours possible?	Reversible: no; only two colours Irreversible: yes	Yes	No
Switching temperature adjustable?	Fixed transition temperatures	Switching temperature is adjustable	Fixed transition temperatures
Colour variable at constant switching temperature?	Fixed colours	Colour variable by changing dye component	Fixed colours
Toxicity	Toxic	Non-toxic	Non-toxic

3.5 Inorganic–Organic Hybrid Materials

Besides the three classes of thermochromic additives discussed previously, hybrid organic–inorganic thermochromic systems are under development in order to combine the advantages of both material classes with one another. A hybrid organic–inorganic thermochromic film is described in [35]. The multilayer film based on polyoxomethalate clusters $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ was prepared by a layer-by-layer self-assembly method. The colour changes gradually from yellowish to blue when it is subjected to temperatures between 120 and 180 °C. Such hybrid materials could be favoured for thermochromic switching temperatures above 100 °C provided that a high transparency in the on and off states is not required.

Hybrid composites of polydimethylsiloxane and gold nanoparticles with an adsorbed monolayer of 1-alcanethiols (1-decanethiol or 1-dodecanethiol) afforded a versatile irreversible colour change [36]. The effect is triggered above 220 °C as a result of desorption of the alcanethiol molecules from the gold surfaces which leads to the irreversible formation of particle aggregates.

Another example of a hybrid organic–inorganic system is described in [37]. Thermochromic properties are obtained by doping a film of polyaniline, poly(*o*-toluidine) and poly(*o*-methoxyaniline) or their polyvinyl alcohol-containing composites with sulfate. Conformational changes are the reason for the temperature-triggered colour change obtained. Poly(di-*n*-hexylsilane)-containing zirconia hybrid thin films show thermochromic properties by transformation of the Si–Si main chain. The preparation was carried out by a sol–gel reaction of di-*n*-hexylsilane–acetoacetoxyethyl methacrylate block copolymers and zirconium alkoxide [38]. A thermochromic polymethyl methacrylate (PMMA)–titania material can be obtained by using acrylic acid or allyl acetylacetone (3-allyl-1,2,4-pentandione) as

coupling agent. The PMMA chains were chemically bonded to the forming titania network [39]. As a final example, a polyvinyl alcohol system is selected. Thermochromic polymer films based on polyvinyl alcohol, variable-valence metals (cobalt, copper, nickel and iron) and orthophosphoric acid are described in [40, 41]. The concentration of metal complexes and also of orthophosphoric acid in the polymer matrix strongly influences the structure of the polyvinyl alcohol–metal ion–orthophosphoric acid complexes formed and thus of the resulting thermochromic properties [40]. Detailed measurements and calculations of the response time of the thermochromic polymer films in reaction to sudden temperature changes were reported and a theoretical background for the calculation of the response time was given. However, no detailed information about the temperature-dependent colour changes of the polyvinyl alcohol–metal complexes has been published.

3.6 Applications

Thermosensitive recording paper was launched onto the market by the National Cash Register Company in 1968. It consists of a paper sheet coated with a single thermosensitive layer comprising leuco dye and developer which are the essential colour-forming components as well as several further additives. By calendaring under high pressure a smooth surface is obtained. Local heating on contact with a thermal pen or thermal head brings the colour-forming components into reactive contact resulting in a distinct image of the heat pattern. The developing temperature of the thermosensitive recording paper can be lowered by the addition of a sensitiser. Then the melting temperature of the sensitiser determines the developing temperature. To prevent adhesion of the coloured leuco dye–developer complexes on the thermal head fillers are added which absorb the coloured melt. Moreover, stabilisers are used to increase the light stability and the long-term storage stability of the recorded images.

Thermochromic inks containing microencapsulated leuco dye-developer are available for all major ink types: water-based and photocuring inks for paper and plastics, epoxy-based inks for glass and wood as well as plastisol inks for textiles. Starting with novelty items such as mood rings in the 1970s, more and more applications are entering the market in which the thermochromic ink becomes a functional part of the product. Battery testers are an example of such a product. Battery testers consist of a printed layer structure. One layer is based on an electrically conductive ink and a second layer on a thermochromic ink. The conductive layer converts the applied voltage into heat. Zones heated above a definite temperature are then displayed by the thermochromic layer.

A current overview of the research and application of smart coatings is given in [42]. Thermochromic layers are also fabricated using ultrasonication, surfactant addition or vapour-phase processing approaches [43].

Textiles manufactured from thermochromic fibres have not entered the market so far. Thermochromics are most conveniently applied to textiles by the screen printing technique using thermochromic inks. They withstand about 20 washings before deterioration becomes visible. Besides new designs, thermochromics enable integration of functionality into textiles [44].

3.6.1 Thermoplastics

Microencapsulated leuco dye-developer-solvent systems as well as polyethylene and polypropylene masterbatches containing them are already commercially available from various manufacturers. Although these masterbatches show excellent thermochromic switching behaviour, the use of microcapsules results in a variety of limitations including poor thermal and shear stability

which cause difficulties in processing. Incorporation of these microencapsulated leuco dye-developer-solvent systems into high-temperature polymers, like polycarbonate, is not possible.

The switching temperature of commercially available microencapsulated leuco dye-developer-solvent systems ranges from -25 to 65 °C. The ambition to extend this temperature range especially towards higher switching temperatures has existed for many years [45]. Although Matsui International were hoping to launch reversible as well as irreversible thermochromic organic pigments with higher switching temperature to the market by 2006, even now no such pigment is commercially available.

3.6.2 Potential Future Applications

The commercialisation of thermochromic polymer materials as functional materials has just started and certainly this market will rapidly grow in the near future. Permanent self-monitoring of the temperature of machine parts to prevent overheating during operation or the displaying of surface temperatures to identify thermal leaks are examples of potential future applications in industrial processing. Smart packages with an irreversible thermochromic colour change could prove the observance of the required temperature conditions during storage or transportation of sensitive goods such as heat-sensitive pharmaceuticals or frozen food. Moreover, thermochromic skin temperature indicators for medical diagnostics might play an increasing role in the future. Addressing of security aspects builds a further potential market. Road signs comprising thermochromic materials could warn of icy conditions. Thermochromic surfaces on heating plates, fire doors, radiators or other domestic appliances that become hot during operation could give an optical non-touch warning that such surfaces are hot.

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Thermochromic Phenomena in Polymers

4 Interaction Between Polymer Matrix and Additive as Origin of Thermochromism

4.1 Crystalline Colloidal Arrays Embedded in Swollen Gel Networks

Monodisperse and highly charged colloidal particles can self-assemble in liquid media of very low ionic strength and form periodic structures at which Bragg reflection occurs. The driving force for the structure formation of the colloidal particles is their electrostatic repulsion.

A colour change with temperature caused by the formation of a crystalline colloidal array in a swollen gel network exhibiting a temperature-induced volume phase transition was reported in [1]. The system presented was obtained by the following two steps. First, highly charged monodisperse polystyrene spheres of 99 nm diameter were dispersed in *N*-isopropylacrylamide solution whereby a self-assembling of the polystyrene colloidal particles into a body-centred cubic structure occurred. Second, a photochemically initiated polymerisation of *N*-isopropylacrylamide was carried out to form a network which permanently locks in the ordering of the crystalline colloidal array. Temperature-induced swelling or shrinking of the polymer matrix results in changes of the lattice spacing of the crystalline colloidal array and thus of the Bragg reflection wavelength. To characterise the thermochromic properties of the novel material, thin films, 125 μm thick at room temperature, were prepared and their Bragg reflection wavelength determined as a function of temperature. Within the temperature range 11.7–34.9 $^{\circ}\text{C}$ a continuous change of the diffracted

wavelength from 704 to 460 nm was measured, which corresponds to nearly the entire visible range. It should be mentioned that the change of the Bragg reflection wavelength is accompanied by a proportional change of the layer thickness. To obtain an increase of the diffracted wavelength from 400 to 800 nm, a swelling in each direction by a factor of two and thus an eightfold increase of the volume has to take place.

Switching a gel below or above a lower critical solution temperature (LCST) is a suitable method to initiate volume changes. By embedding a crystalline colloidal array with appropriate lattice spacing, the volume changes are accompanied by thermochromic effects. A crystalline colloidal array of silica spheres (diameter 210 nm) in a copolymer electrolyte hydrogel of methacrylic acid, *N*-isopropylamide and *N,N'*-methylene bisacrylamide as crosslinker has been described. The gel matrix exhibits different equilibrium degrees of swelling depending on pH as well as on temperature. If the pH-sensitive hydrogel is placed on electrodes the degree of swelling can be easily and drastically changed by electrolysis. A sufficient voltage, high enough to electrolyse water, is required for this effect. It was found that the electrochemically controlled pH value indeed causes a two-state thermochromic switching phenomena of the investigated porous hydrogel system [2, 3].

The intensity of the Bragg reflection of crystalline colloidal arrays depends on the array ordering as well as on the scattering cross-section of the colloidal particles which is influenced by their size. The preparation of highly charged and monodisperse colloidal particles of poly(*N*-isopropylacrylamide) (PNIPAM) with a size of 100 nm is reported in [1]. Dispersed in water the PNIPAM colloids self-assemble and form a body-centred cubic array. In water PNIPAM exhibits a LCST of about 32 °C. Below this temperature PNIPAM is hydrated. It incorporates water into the network structure transforming thereby into a hydrogel. This

reversible process is accompanied by swelling. With decreasing temperature the water content of the PNIPAM hydrogel increases. Accordingly, the sphere diameter of the PNIPAM colloidal particles dispersed in water increases also. Whereas above 32 °C the sphere diameter remains unaffected by the dispersion in water, it increases on cooling from 32 to 10 °C by a factor of 3. As an example, the optical properties of a crystalline colloidal array of PNIPAM colloids (diameter of 100 nm) in deionised water with a lattice constant of 342 nm were reported. Thermochromism occurs below 32 °C in the form of a change of colour intensity with temperature. At 40 °C the nearest neighbour sphere distance amounts to 242 nm and at the Bragg reflection wavelength nearly all incident light is reflected. At 10 °C, in contrast, the PNIPAM colloids have a diameter of 300 nm. They are almost touching and only a weak Bragg reflection occurs. Since the lattice spacing of the cubic array depends only on the particle density and not on the particle size, the wavelength of the Bragg reflection remains unaffected by the reversible swelling or shrinking of the PNIPAM particles.

4.2 Dyes Embedded in Polymer Gel Networks

A thermochromic effect of pH-indicator dyes incorporated in a transparent hydrogel matrix was first reported in [4]. The matrix used was a polyvinyl alcohol (PVA)–borax–surfactant hydrogel network. A thermochromic effect was observed if an indicator dye having a pK_a value between 7.0 and 9.4 was added, with the precondition that the indicator dye was soluble in the hydrogel matrix. With increasing temperature the phenol/phenolate equilibrium of the investigated indicator dyes was shifted towards their deprotonated forms. The Reichardt betaine dye: 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate (DTPP) is colourless in the phenol form and violet in the phenolate form. By adding this dye to the PVA–borax–surfactant hydrogel a gradual colour change from colourless at 10 °C to a deep violet at 80 °C was observed

for the thermochromic hydrogel obtained. Cresol red is yellow in the phenol and wine-red in the phenolate form. Consequently, by using this dye a thermochromic hydrogel switching from yellow at 10 °C to wine-red at 80 °C was obtained. Visible absorption measurements carried out at various temperatures for both these indicator dye-containing PVA–borax–surfactant hydrogels confirm the model of a temperature-dependent equilibrium between the phenol and phenolate form of the indicator dye as the origin of the thermochromic effect. In the case of the cresol red-containing PVA–borax–surfactant hydrogel both the phenol and phenolate form of the indicator dye were detected. On heating from 10 to 80 °C a continuous increase of the intensity of the absorption band at 581 nm, which corresponds to the phenolate form of cresol red, is observed while simultaneously the intensity of the absorption band at 419 nm, which corresponds to the phenol form, decreases. No shift of the absorption maximum takes place and all spectral curves meet at an isosbestic point at 486 nm. Similar behaviour is reported for thymol blue embedded in an analogous hydrogel system [5], the absorption spectra for which are shown in **Figure 4.1**. On heating a switch from yellow to green takes place due to a simultaneously occurring intensity decrease of the absorption at 438 nm and intensity increase of the absorption at 605 nm. An isosbestic point is located at about 500 nm.

Thermochromic PVA–borax–indicator dye hydrogels without additional surfactant are described in [6]. Instead of a surfactant, *n*-butanol was added to dissolve all components in the system. By using the indicator dye phenolphthalein a switch from colourless to red and by using bromothymol blue from green to blue was observed on heating the obtained hydrogels from 20 to 70 °C.

The construction of a gel consisting of dye, polymer, crosslinker and additional components like surfactants or an aliphatic alcohol is extremely sensitive and complex. In fact, it is generally known that PVA itself exhibits surfactant properties in water.

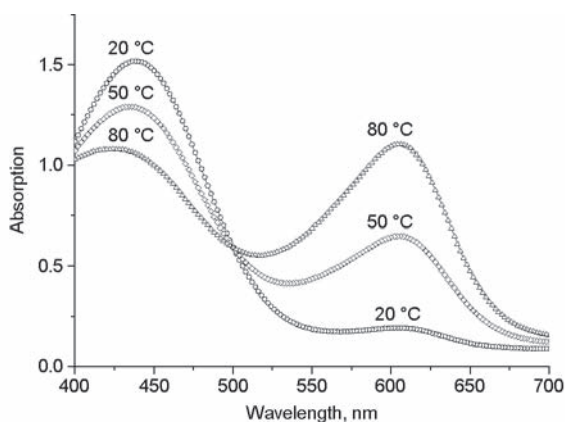


Figure 4.1 Absorption spectra of a thymol blue-containing PVA-borax-surfactant hydrogel at different temperatures ($d = 5$ mm)

This means that even the thermochromic hydrogels described in [6] are not surfactant free. In the aqueous environment of the PVA-borax-indicator dye hydrogels, an intermolecular interaction between the organic hydroxyl groups of PVA and of *n*-butanol can be expected leading to the formation of a typical surfactant/co-surfactant system. Thus it can be assumed that *n*-butanol acts as a co-surfactant in the hydrogel system similar to its behaviour in an aqueous PVA solution [7].

A thermochromic effect occurring on the addition of a pH-indicator dye to a hydrogel matrix was also observed in polyalkoxide-LiCl systems. In these systems additionally a thermotropic switching effect occurs. Such gel networks for reversible transparency and colour control with temperature are separately discussed in Section 5.2.3. An overview of the reported thermochromic hydrogels and their temperature-dependent colour changes is given in **Table 4.1**.

Table 4.1 Thermochromic hydrogels and their temperature-dependent colour or colour intensity changes			
Hydrogel matrix	Indicator dye	Colour or colour intensity changes on heating from 5 to 80 °C	Reference
PVA-borax	2,6-Diphenyl-4-(2,4,4-triphenylpyridinio)phenolate (DTPP)	Colourless-violet	[4]
PVA-borax	Cresol red	Yellow-wine red	[4]
PVA-borax	Phenol red	Yellow-purple	[8]
PVA-borax	Thymol blue	Yellow-green	[5]
PVA-borax	Phenolphthalein	Colourless-red	[6]
PVA-borax	Bromothymol blue	Green-blue	[6]
PVA-borax	Bromothymol blue and cresol red	Yellow-green-violet	[9]
Polyalkoxide-LiCl	Chlorophenol red	Red-yellow	[10]
Polyalkoxide-LiCl	Nitrazin yellow	Blue-green	[10]
Polyalkoxide-LiCl	Bromothymol blue	Green-yellow	[10]

Simple two-component systems consisting of an indicator dye and Nafion (perfluorosulfonate ion-exchange polymer) exhibit thermochromic behaviour [11]. The strongly acidic nature of Nafion can be utilised in a Nafion–crystal violet film [12] in which the crystal violet was found to be in its deprotonated form. The observation of thermochromic Nafion systems is described in [11]. Dye solutions in ethanol with concentrations of either 0.02 or 0.002 g/ml were prepared. A small volume of a Nafion solution (5 wt% in low alcohols containing 10 wt% water) was cast onto an acetate sheet and immediately the same volume of dye solution was added. The mixture was gently homogenised and allowed to dry. Tested films containing the pH-indicator dyes safranin-O, phenolphthalein and methylene blue showed thermochromic behaviour. The crystal violet film, in contrast, was sensitive to moisture but did not show any sensitivity to temperature within the investigated temperature range from 2 to 70 °C. Marked thermochromic behaviour was observed for the phenolphthalein–Nafion system. The colourless form is present at ambient temperature (20 °C). On heating an absorption band with a peak maximum at 505 nm appears and the film becomes pink. With increasing temperature the absorption intensity increases. At 30 °C an absorbance value of approximately 0.7 and at 70 °C of approximately 1.3 is achieved. However, the film thickness of the investigated film was not reported. Below 20 °C the film remains colourless. The pink form of phenolphthalein is its deprotonated state which is the dominant species in aqueous solution when the pH-value is larger than 9.3. The increased concentration of this form of the dye suggests that the microenvironment becomes less acidic with increasing temperature. This corresponds to the behaviour of pH-indicator dyes in PVA–borax hydrogel networks [4].

A temperature- and CO₂-sensing pH-indicator dye-containing polymer film sensor is reported in [13]. The polymer film, which was prepared by casting polymer solution on a glass substrate, is composed of a pH-indicator dye, a phase transfer agent, a

polymer and a plasticiser. The function of the phase transfer agent (tetraoctylammonium hydroxide) is to solvate the hydrophilic indicator dye (phenolphthalein) in the hydrophobic polymer matrix (ethyl cellulose) and to provide the trace water required to allow dissolution of CO₂ in the system. At room temperature and atmospheric CO₂ levels (3×10^{-4} atm) the phenolphthalein in the polymer film sensor is mostly in its protonated colourless form. With increasing temperature and/or increasing CO₂ concentration the equilibrium between the protonated and deprotonated forms of phenolphthalein shifts towards the deprotonated deep pink species.

4.3 Applications

Neither crystalline colloidal arrays nor thermochromic hydrogels have found any commercial application so far. Thermochromic effects based on changes of the pH value find their application in medicine techniques as well as in hygiene products [14].

From the applications point of view crystalline colloidal arrays have attracted more interest because of their ionochromic rather than their thermochromic properties. The ionochromism is achieved by the incorporation of molecular recognition agents into polymerised crystalline colloidal arrays. Lead ion (Pb²⁺) and glucose sensors have been reported [15, 16].

The outstanding properties of thermochromic hydrogels are their transparency and the possibility to switch from colourless to coloured on heating. Another important feature is that the thermochromic effect is not accompanied by volume changes, which is a necessary condition for the application in smart windows, large-area displays and tunable colour filters. Despite their excellent thermochromic properties, no commercial product based on thermochromic hydrogels has been brought onto the market so far.

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5 Thermotropic Polymer Systems

The term thermotropic denotes a change of the light-scattering properties of a system with temperature. This subclass of thermochromic materials changes transparency but not colour with temperature. Depending on temperature, switching between a highly transparent and a light-scattering milky white state takes place. Thermotropic effects can be caused by a phase separation process, by a phase transition between an isotropic and an anisotropic (liquid crystalline) state or by a different temperature dependency of the diffractive indices of a two-phase guest–host system. In recent years the thermotropic properties of polymer blends, polymer hydrogels and casting resins doped with an additive which forms a separate phase have been extensively studied.

5.1 Polymer Blends

An uninterrupted miscibility of binary polymer systems is quite unusual. Miscibility gaps occur in most phase diagrams. Certain binary polymer systems exhibit critical solution temperatures, whereby with increasing temperature an increase or a decrease of the miscibility can occur. Polymer systems with an upper critical solution temperature (UCST) are uninterrupted miscible with one another above the critical solution temperature and possess a miscibility gap below the UCST. A lower critical solution temperature (LCST), in contrast, denotes an uninterrupted miscibility at low temperatures and a miscibility gap above the LCST. Within wide concentration ranges the polymer blends

of such systems are thermotropic. On heating a thermotropic polymer blend of a polymer system with a LCST a transition from a transparent to a light-scattering milky white state occurs. Thermotropic polymer blends of systems with an UCST switch in the opposite manner. Because of their potential application for sun-protecting glazing the development of thermotropic polymer blends has focused in recent years on systems with LCST.

Thermotropic polymer blends composed of a chlorinated rubber and polymethacrylates were developed in 1993 (Röhm GmbH) [1]. Depending on the composition, the cloud point, which denotes the transition temperature from the transparent to the translucent state, could be adjusted within the temperature range 60–140 °C. For applications in sun-protecting glazing cloud points between 30 and 40 °C are required. Thermotropic polymer blends with cloud points in this temperature region were presented in the same year [2]. Moreover, in comparison to the chlorinated rubber–polymethacrylate blends an improved reversibility of the thermotropic switching was obtained. The polymer blends presented were derived from mixtures of polypropylene oxide and a styrene–hydroxyethyl methacrylate copolymer which was cross-linked with a trifunctional cyclic isocyanate. The semi-interpenetrating network formed by the crosslinking of the copolymer leads to an increase of the stability of the microphase separation above the cloud point. Consequently, an improved reversibility of the thermotropic switching is obtained. A similarly cross-linked thermotropic polymer blend was developed in 1995 by BASF [3]. However, the crosslinking reaction was carried out by photopolymerisation instead of chemically by adding a crosslinking agent. A mixture consisting of polypropylene oxide, a styrene copolymer, hydroxyethyl methacrylate and a small amount of 4-acroyloxybutylcarbonatobenzophenone was prepared and afterwards cross-linked by exposure to UV light. The advantage of this method is the better processability of the material before the

semi-interpenetrating network is formed. By this method, coatings with an improved evenness of their surfaces and thus of their optical quality were obtained. The optical properties of thermotropic glazings based on the two polymer blends described in [2, 3] are presented in [4, 5]. A glazing coated with a 400 μm layer of the chemically crosslinked polymer blend [3] changes the integrated normal hemispherical transmission from 92% at 20 °C to 30% at 90 °C. Similar results were obtained for a glazing coated with a 600 μm layer of the polymer blend prepared by crosslinking using UV light [3]. This glazing changes the integrated normal-hemispherical transmission from 89% at 30 °C to 38% at 85 °C.

5.2 Thermotropic Polymer Gel Networks

Thermotropic polymer gels can be based on the appearance of lyotropic liquid crystalline phases, on phase separation processes or on changes of the refractive index of dispersed particles. Similar to the behaviour of polymer blends, polymer gels can also exhibit lower and upper critical solution temperatures in their phase diagrams. The potential application in sun-protecting glazing has stimulated the material development of polymer gels switching from transparent to light-scattering on heating.

Since their first observation, lyotropic liquid crystalline polymers like polybenzyl glutamate (PBLG) [6, 7], hydroxypropyl cellulose (HPC) [8, 9] and full-aromatic polyamides [10] have been extensively studied. All these polymers are highly soluble in water and their molecular structures consist of a more or less rigid polymer backbone (stiff chain of polymer). In certain concentration ranges of binary mixtures with water or certain organic solvents these polymers undergo a transition from an isotropic phase to a polymer-solvent system with pronounced long-range order. This transition is accompanied by a change from a transparent into a light-scattering state.

The thermotropic properties of lyotropic liquid crystalline polymer hydrogel networks are reported in [11]. Lyotropic liquid crystalline phases were found to appear in a hydrogel obtained by crosslinking a solution of an epoxylated PVA with borax as well as in similar gels in which the epoxylated PVA was substituted by a binary mixture of polyethylene glycol and PVA. Within wide concentration ranges the prepared hydrogels were found to possess thermotropic properties. On heating from the lyotropic liquid crystalline into the isotropic liquid phase, a change of the optical appearance of the hydrogels from a milky white light-scattering to a clear state occurs, which is accompanied by a change of the transparency. Transparency changes from below 5% at low temperatures to more than 70% above the respective clearing temperature and contrast ratios of up to 85:1 were measured. Microscopic observations of schlieren and radial-droplet structures between crossed polarisers revealed that the formation of lyotropic liquid crystalline phases is the origin for the appearance of light-scattering states. The influence of concentration and molecular masses of both polymers as well as of the degree of crosslinking on the thermotropic properties was studied. An increasing PVA concentration and an increasing molecular mass of the polyethylene glycol used were found to lead to a shift of the clearing point and thus of the thermotropic switching temperature towards higher temperatures. Clearing temperatures between 30 and 90 °C were reported for the investigated PVA–polyethylene glycol–borax hydrogel networks. In all samples the lyotropic liquid crystalline to isotropic phase transition does not influence hydrogel network formation. Thus the mechanical properties remain unaffected by the optical switching process.

Phase separation processes in polymer gel networks have been well known for a long time. In the following paragraphs we will focus on recent developments in the preparation of thermotropic polymer gel networks based on synthetic polymers, on biopolymers and

on polymer gel networks that combine thermotropic and colour changing properties. Moreover, the construction of hybrid solar and electrically controlled light filters is reviewed.

5.2.1 Thermotropic Polymer Gel Networks Based on Synthetic Polymers

Gels consist of a swollen polymer network in which a solvent component is incorporated. The network formation can be carried out either by a chemical reaction (chemical gels) or by complex formation (physical gels) between the polymer chains and the crosslinker. In chemical gels the polymer chains are crosslinked by covalent bonds. In contact with the solvent component chemical gels generally strongly swell or shrink with temperature. Phase separation processes of such gels are also accompanied by distinct volume changes. In contrast to chemical gels, physical gels are formed by non-covalent interactions between crosslinker and polymer chains. Polar–polar interaction, disperse–disperse interaction and/or hydrogen bonding can contribute to the network formation. Typical crosslinkers for physical gels are borax, salts, phosphonic acid and its derivatives as well as alcohols. Phase separation processes in physical gels are often not accompanied by volume changes. This is an essential condition for their application as functional optical materials in closed systems such as a sun-protecting glazing assembly.

With a view to commercial application the development of thermotropic polymer gel networks has focused on hydrogels. Water-soluble polymers like polyacryl acid derivatives, polyvinyl alcohol, polyglycol, polyvinyl acetal resins, polyethers and cellulose derivatives have been successfully used as polymeric starting materials. The most investigated chemical crosslinked hydrogels with thermotropic properties are poly(*N*-isopropylacrylamide) homo- and copolymers [12–16]. Poly(*N*-isopropylacrylamide) was

the first reported non-ionic hydrogel exhibiting a thermoresponsive volume phase transition. As found in 1984 the poly(*N*-isopropylacrylamide) hydrogel transforms on heating at about 34 °C from a gel state into a collapsed solid state [12]. This reversible transition is accompanied by a distinct volume change and by a switching from a highly transparent into a translucent state. Investigations of the optical properties of the poly(*N*-isopropylacrylamide) hydrogel are presented in [16]. Despite the fact that the distinct volume change of this hydrogel disables it for commercial use in sun-protecting glazing, a non-sealed adaptive gel-glass assembly comprising a poly(*N*-isopropylacrylamide) layer was also constructed. The two glass substrates are only fixed by adhesion on the hydrogel surface, so that the layer spacing changes in response to thickness changes of the hydrogel layer. Transparency changes from more than 95% to less than 1% were reported for a glazing assembly comprising a layer of poly(*N*-isopropylacrylamide) with a thickness of 1 mm in the gel state. The mechanical stress appearing on passing the collapse transition temperature leads to the formation of a surface pattern. It was stated that the establishment of strong adhesion between gel and glass surfaces might eliminate this phenomenon. However, the mechanical forces are still present.

In 1995 a thermotropic hydrogel based on poly(methyl vinyl ether) crosslinked with methylene bisacrylamide [17, 18] was presented. The so-called Cloud Gel™ is commercially available from Suntek Corporation. Depending on the composition the switching temperature can be varied within the temperature range 10–65 °C. Investigations of the temperature dependence of the optical properties of Cloud Gel™, including measurements of the integrated normal-hemispherical transmission, were carried out [4, 19]. For a 1 mm thick layer of Cloud Gel™ the integrated normal-hemispherical transmission in the visible range was found to change reversibly between 92% at 25 °C to 6%

at 50 °C. Moreover, high contrast ratios were observed for the transmission *versus* temperature curves. Already one degree above the transition temperature a transmission reduction of about 65% occurs. Compared to polymer blends, Cloud Gel™ shows enlarged transparency changes and contrast ratios.

Physical thermotropic hydrogels with excellent switching properties were also developed [20–22]. The reported thermotropic hydrogel systems are based on polyalkoxides composed of ethylene oxide and propylene oxide units which were physically crosslinked by salts or other complex-forming compounds. These systems tend to have an anisotropic phase and also possess lower critical solution temperatures. Depending on the ethylene oxide to propylene oxide ratio of the polyalkoxide and the kind of crosslinking agent, switching temperatures from the low-temperature transparent state into the high-temperature light-scattering state between room temperature and 80 °C were obtained. The contrast ratios of the investigated hydrogels were found to be comparable with those of Cloud Gel™, and as expected for physical gels no swelling or shrinking with temperature was observed. Detailed investigations of the influence of the crosslinking salt used on the phase separation temperature are reported in [21]. Comparing the effect of different salts on the shifts of the phase separation temperatures at a constant concentration, a ranking according to the so-called Hofmeister series, which is a measure for the salting-in or salting-out strength of salts, was found. By using salts with a salting-in effect an increase of the phase separation temperature occurs, while salts with a salting-out effect have the opposite effect. The influence of LiCl on gel formation, polymorphy, water binding properties as well as on the rheological and thermo-optical behaviour of one of these hydrogel systems is reported in [22]. In certain concentration ranges the appearance of anisotropic phases was observed. These hydrogels possess multiple minima and/or maxima in their transmission versus temperature curves.

A thermotropic effect caused by water-dispersed nanoparticles which vary their size with temperature is reported in [23]. The nanoparticles used consist of a polystyrene core encapsulated with poly(*N*-isopropylacrylamide). In water poly(*N*-isopropylacrylamide) forms a gel which exhibits a LCST of about 31 °C. On heating above the LCST the hydrophilic–hydrophobic balance is suddenly changed and the gel shrinks. By this effect the particle size of the water-dispersed polystyrene–poly(*N*-isopropylacrylamide) core–shell nanoparticles is reduced from about 1000 to about 430 nm. The shrinking is accompanied by a change of the refractive index of the nanoparticles and thus by a change of the light-scattering properties of the water dispersion. Below the LCST a weak and above it a strong light-scattering effect was observed for the investigated water-dispersed nanoparticle system. Through inking of the polystyrene core with a blue dye the investigated nanoparticles were coloured. Passing through the LCST is reported to have a drastic effect on the colour intensity of the dispersion. The dispersion appears intensely blue at room temperature and gradually pales as the temperature rises above 31 °C. This effect is called ‘thermotropic colour change’ by the authors. It would be more appropriate if the authors discussed the visual effect as a change of the transmittance concealing the colour in the state of low transmittance and not as a colour change.

5.2.2 Thermotropic Polymer Gel Networks Based on Biopolymers

Compared to most synthetic polymer materials biopolymers have the advantage of their biodegradability. The pool of biopolymers contains non-toxic and inexpensive raw materials which are commercially available in large quantities, as for example cellulose derivatives or polysaccharides. The suitability of biopolymers as starting materials for the preparation of thermotropic hydrogels

was demonstrated in [24]. Aqueous solutions of cellulose derivatives and an amphiphilic component were crosslinked by the addition of various amounts of NaCl. Depending on the composition, thermotropic polymer networks with switching temperatures between room temperature and 60 °C were obtained. The function of the amphiphilic component is to prevent an irreversible flocculation of the cellulose derivative. A 1 m² prototype of a sun-protecting glazing comprising one of these thermotropic polymer materials was constructed and successfully tested under practical conditions over a period of two years.

Thermotropic hydrogels based on cellulose derivatives were also presented in [25]. By using a mixture of hydroxypropyl cellulose and hydroxyethyl cellulose, even without adding an amphiphilic component reversible thermotropic switching was obtained.

5.2.3 Gel Networks for Reversible Transparency and Colour Control with Temperature

Polymer gel networks possessing in one material thermotropic switching from a transparent to a light-scattering state and thermochromic colour changes with temperature were recently developed [26]. These materials were termed chromogenic. Both effects, the transmission and the colour change with temperature, do not interact with one another. They can be adjusted independently. The development comprises two strategies: modifying thermotropic hydrogels, thus additionally becoming thermochromic, or modifying thermochromic hydrogels, thus additionally becoming thermotropic.

A thermotropic polyalkoxide–LiCl hydrogel formulation was modified by replacing the water component through a buffer solution and by adding one of the pH-sensitive indicator dyes chlorophenol red, nitrazine yellow or bromothymol blue. These

changes of the composition were found to have only slight influences on the thermotropic phase separation process of the hydrogel matrix, but led to the appearance of thermochromism. Similar to the thermochromic effect of PVA–borax–surfactant gel networks [27], the colour change was explained by temperature-induced pH changes of the gel network. However, with increasing temperature a stabilisation of the phenol form was observed in the polyalkoxide–LiCl gel networks, which is in contrast to the behaviour of phenol-substituted indicator dyes in a PVA–borax–surfactant gel network, where the opposite effect was found. Depending on the specific gel network used, the pH-sensitive phenol/phenolate equilibrium can be obviously shifted with temperature in both directions. No explanation for this effect has been published so far. As an example, the thermo-optical properties of an hydrogel prepared by mixing 3.95 g polyalkoxide, 0.25 g LiCl, 0.8 g of an aqueous buffer solution (pH = 10) and 0.12 g of a 2.2% aqueous solution of bromothymol blue were reported. On heating this hydrogel from room temperature to 33 °C a gradual colour change from green to yellow occurs. With increasing temperature a shift of the pH-sensitive equilibrium from the green phenolate to the yellow phenol form of bromothymol blue takes place. In the absorption spectra this colour change is displayed by a cross-over between an absorption band at $\lambda = 408$ nm and one at $\lambda = 617$ nm. On further heating above 36 °C the hydrogel again changes its appearance. The yellow transparent state transforms into a yellow translucent state. The transparency decreases from above 80% to less than 1%.

The introduction of thermotropic properties in a thermochromic phenol red-containing PVA–borax–surfactant hydrogel is reported in [28]. The thermotropic effect which is based on a phase separation process was introduced by adding small amounts of a polyalkoxide. The polyalkoxide used is more hydrophobic than PVA. At a polyalkoxide concentration as small as 0.8 wt%

the appearance of a phase separation process on heating was observed while the thermochromic colour change remained almost unaffected. On heating from 10 to 80 °C the colour of the hydrogel gradually changes from yellow to purple. With further increasing polyalkoxide concentration in the system the rate of the transparency change with temperature is increased and takes place at lower temperatures. At a concentration of 1.5 wt% the transparency changes from about 90 to 20% within the temperature range 20–30 °C.

As a variation of the concentration of the zwitterionic sulfobetaine surfactant shows, the surfactant influences both the thermotropic and the thermochromic switching behaviour. The investigations were carried out on PVA–borax–phenol red hydrogels containing 1.1 wt% polyalkoxide. Various sulfobetaine concentrations below and above the critical micelle concentration ($\text{CMC} = 3.8 \times 10^{-3} \text{ mol/kg}$) were added to the system. The thermochromic behaviour was characterised by absorption spectroscopy in the range 350–700 nm and a transparency change was detected at 750 nm where the system shows no absorption. Two absorption peaks were observed in the visible range, one at $\lambda = 440 \text{ nm}$ corresponding to the phenol form of phenol red and the other at $\lambda = 563 \text{ nm}$ corresponding to the phenolate form. The intensity of both UV–visible absorption bands decreases as the sulfobetaine concentration is increased. This effect is already observed at the lowest sulfobetaine concentration of $2.5 \times 10^{-3} \text{ mol/kg}$, which is significant below the CMC. Although it is well known that surfactants above their CMC can influence the UV–visible absorption behaviour of water-soluble dyes, the occurrence of such an effect below the CMC is remarkable. As for the thermochromic effect a small but significant and reproducible influence of the surfactant concentration on the thermotropic behaviour is also reported to occur even below the CMC. Two alternative models are discussed to explain these effects: (a) the formation of complexes between dye molecules and aggregates

of sulfobetaine; and (b) an interaction between dye and single sulfobetaine molecules.

5.2.4 Hybrid Solar and Electrically Controlled Light Filters

The construction of a glazing assembly with changing transmission which switches either passive by temperature changes or active by an applied electric voltage is described in [29]. It consists of two tin-doped indium oxide (ITO)-coated glass substrates covering a layer of a thermotropic hydrogel with a thickness of 2–3 mm. The positions and thicknesses of the ITO layers were varied. ITO layers of 1330, 4160 or 5800 Å thickness were arranged either at the inside (between glass and hydrogel) or at the outside of the glazing assembly. Depending on the thickness of the ITO layer, a resulting sheet resistance of 4–16 Ω /square was obtained. When heated passive by temperature changes of the environment or active by applying an electric voltage on the ITO layers the thermotropic hydrogel switches from the transparent to the light-scattering state. The influences of the construction of the glazing assembly as well as of the thermochromic hydrogel material used on the switching characteristics of the glazing items were investigated. Transmissions *versus* time curves as a function of the applied voltage were determined. No electrolysis was observed under the experimental conditions even for the glazings where ITO and hydrogel layers were in direct contact. An increase of the ITO layer thickness reduces the transparency of the glazing assembly but results in a faster switching time at a constant applied voltage. On applying a wattage of 0.246 W/cm² one of the glazing assemblies was found to change transmission from about 62% to $\leq 1\%$ within a switching time of 5 min.

It was concluded that a further significant reduction of the required wattage could be achieved by optimising construction

and all components of the glazing. This includes, in particular, specific material development of a thermotropic hydrogel with a low heat capacity.

5.3 Thermotropic Casting Resin

A thermotropic casting resin composed of a photocuring matrix polymer system and an immiscible monomeric additive is described in [30]. The monomeric additive which forms a separate phase in the cured matrix polymer exhibits a discontinuous change of refractive index with temperature due to structural rearrangements. The refractive index of the matrix polymer, in contrast, remains nearly constant with temperature. By using a pair of matrix polymer system and additive whose refractive indices at low temperatures are equal, a thermotropic casting resin switching from a transparent to light-scattering state on heating is obtained.

Suitable monomeric additives for the thermotropic casting resin are long-chain aliphatic compounds, especially alkanes with a chain length of 10–25 carbon atoms. Depending on the additive used, various thermotropic switching temperatures within the temperature range 10–50 °C could be realised.

5.4 Applications

As for the other thermochromic materials, thermotropic polymers can be applied either as temperature sensors or as temperature-controlled light filters. In contrast to the potential future applications of colour-changing thermochromic materials, the interest in thermotropic materials appears more because of their thermo-optical properties than of their ability to detect temperature changes. Thermotropic materials are not only light shutters for visible light but also for heat radiation. In the light-scattering state a large portion of the light radiation energy is reflected and

does not cause heating of the thermotropic layer. These optical properties favour thermotropic materials for use as functional layers in sun-protecting glazings [31, 32].

In addition to the classic function of glazings as a transparent facade element enabling a view to the outside of buildings, glazings have become high-tech components in modern architecture. Incident solar radiation is used for the internal illumination of buildings and the solar energy reduces the energy consumption for space heating. The illumination of buildings with daylight contributes to the wellbeing of the occupants. Besides viewing windows, large-area illumination windows, skylights and sunroofs have become part of modern buildings. In quite a lot of buildings glazing elements have even reached a proportion of larger than 80% of the facade area. Incident solar radiation plays an increasingly important role in the energy balance of buildings as the percentage of transparent facade elements increases. Whereas incident solar energy reduces the energy consumption for space heating on cold days, it causes an overheating of the inside of buildings and thus an enormous increase of the energy consumption for space cooling on hot days. As a result the energy consumption for space cooling can even exceed that for space heating.

To reduce the incident solar radiation on demand, mechanical optical shutters like Venetian blinds, awnings and sun blinds are used. A better solution is to adjust the optical properties of the glazing either actively or automatically according to changes in climatic conditions. Such so-called smart glazings are based on chromogenic materials. Automatically adjusting smart windows comprise a layer of a thermochromic or thermotropic material.

Thermochromic coatings of vanadium dioxide are at present the most commercially used thermochromic material for sun-protecting glazings. Detailed treatments of vanadium dioxide and also of electrochromic multilayer structures are given in [33, 34].

Sun-protecting glazings in which a functional layer of a thermotropic polymer material is incorporated into the glazing assembly have the potential to outperform vanadium dioxide-coated glazings. Although the development of thermotropic glazings started more than 50 years ago, none of the presented prototypes have yet been launched onto the market.

A prototype of a sun-protecting glazing based on a thermotropic polymer material was formulated in 1950 and tested in the residence of the Munich zoo over a period of about 10 years. It consisted of the gel network 5 wt% of poly(vinyl methyl ether) in agar-agar, sandwiched between a double glazing. Although the test demonstrated the feasibility of a thermotropic glazing, the transparency change was insufficient for commercial use. Thermotropic hydrogels with strongly improved optical properties and advanced prototypes of sun-protecting glazings containing them have been presented [17, 18, 20, 24]. Transparency changes from above 90% in the transparent state to below 10% in the translucent state were obtained and the switching process takes place homogeneously without the appearance of streaks. The glazing presented in [24] is based on a biopolymer. Although biodegradability is often stated to be an advantage of biopolymers, it also causes restrictions for their commercial use because any contact of the biopolymers with microorganism during the production process and also during the total life time of the glazing must be prevented.

Commercial production of thermochromic glazing based on hydrogels requires a technology transfer from laboratory manufacturing to an industrial production process. An automated production line for putting the polymer between the double glazings has to be developed.

Compared with electrochromic glazing, smart windows based on thermotropic hydrogels have the advantages of lower costs and a much higher transparency in the clear state. However, specific

applications require switching on demand. The hybrid solar and electrically controlled light filters presented in [29] enable active switching of thermotropic hydrogels without impairing the optical properties too much.

A sun-protecting glazing, T-Opal[®], based on a thermotropic casting resin [30] has been developed by the Fraunhofer IBP. T-Opal[®] consists of a double float glazing with the thermotropic casting resin in between. Attempts for commercial production of T-Opal[®] by Okalux have been deferred.

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6

Concluding Remarks

Two things should be accentuated once more in detail: questions of definitions in order to ensure a clearly marked scientific declaration of the effects as well as possible developments in the future.

The terms thermochromic and thermotropic, used for a verbal description of macroscopic visible effects, are unfortunately sometimes used incorrectly. This is the point of origin for misunderstandings and misinterpretations. Even published papers are not accurate [1–4].

In [4] the headline describes thermotropic colour-changing nanoparticles. In this connection a change of colour from deep blue at room temperature to a much lighter pastel blue as the temperature is increased above the LCST is discussed. However, no colour change – no changes of the wavelength maximum – takes place. A pure thermotropic effect leads to a variation of the translucence of the system. It is not correct to use the term colour change in this context.

An electro- and thermochromic hydrogel as a full-colour indicator is presented in [2]. A common electrolysis of an aqueous medium, which is accompanied by changes of the pH-value is called electrochromism. The use of the term electrochromism in this content seems to be incorrect. The term electrochromism is clearly defined. An electrochromic material is characterised by its ability to sustain reversible and persistent changes of optical properties when a voltage is applied to it [5, 6].

In [1] the preparation and characterisation of thermochromic fibres are reported. The detection of the thermochromic effect of the fibres obtained is described only by DSC measurements. DSC measurements detect the thermal behaviour of the incorporated leuco dye–developer–solvent systems. A discussion of optical properties in this context is not admissible.

The last example selected concerns [3]. The headline presents a surfactant-free thermochromic hydrogel based on a PVA–borax network. It is well established that PVA acts as a non-ionic surfactant itself [7].

Without any question all contributions and helpful suggestions to develop the topic are welcome. These remarks aim only to sharpen the view for critical reading of the literature and for using the correct terms.

It can be expected that future developments pose a challenge. However, the suggestion is that in the next few years the commercialisation of thermochromic polymers will make a big step forward. From the point of view of the authors, research and development work will focus on the following improvements of organic thermochromic systems:

- Improvements of the thermal and mechanical stability of thermochromic pigments for the doping of polymer matrices.
- A considerable increase of the UV and visible light stability of leuco dye–developer–solvent systems.
- An extension of the switching temperature range of thermochromic pigments especially above the currently existing limit of 69 °C for commercial products.

- Inverse thermochromic switching from a colourless to a coloured state on heating. Reported examples of systems with such a thermochromic switching behaviour are only of academic interest [8–10]. A first practicable solution is described in [11].
- Deposition of organic thermochromic layers on the surfaces of substrates by vacuum techniques (thermal vacuum vaporisation, sputtering, chemical vapour deposition, organic phase vapour deposition) as is already used for inorganic thermochromic materials. First laboratory samples could be developed [12].
- Comprehension of thermochromic materials in displays, devices, modules or electro-optical equipment of any kind [13, 14].

In general, knowledge about the resulting material properties of the final polymer products has to be enhanced. The doping of polymer matrices with thermochromic additives should not lead to a quality impairment of any material properties such as E-modulus and bending strength. This aspect has not really received adequate consideration up to now [15].

Step-by-step these developments will establish new areas of commercial applications [16]. For example, the use of thermochromic materials (a) with light stability for outdoor applications; (b) in highly thermally stressed functional materials; (c) in extrusion processes of high-temperature polymers such as polycarbonate or polyethylene terephthalate; (d) for multiple temperature indicating heat sensors comprising thermochromic and inverse thermochromic switching pigments; and (e) in thermochromic hybrid organic–inorganic layered structures produced by vapour deposition.

For the particular application of thermotropic polymer materials in sun-protecting glazing, further efforts to improve the rate of the transparency change between on and off modes are necessary [17].

The primary literature clearly emphasises the rapidly growing interest in thermochromic pigments, thermochromic materials with a focus on thermochromic polymer materials and finally in commercial products possessing thermochromic properties.

The authors are confident that the future will bring a series of fascinating findings and developments in the field of thermochromic polymers and the entire spectrum of stimuli-responsive materials. A colourful time with thermochromism can be expected.

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Abbreviations

BCMU	Poly(<i>n</i> -butoxycarbonylmethylurethane)-diacetylenes
BPA	Bisphenol A
CMC	Critical micelle concentration
CTAB	(<i>N</i> -cetyl- <i>N,N,N</i> -trimethylammonium bromide)
CVL	Crystal violet lactone
DETA	Diethylene triamine
DSC	Differential scanning calorimetry
DTPP	2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate
HOMO	Highest occupied molecular orbital
HPC	Hydroxypropyl cellulose
IR	Infrared
ITO	Tin-doped indium oxide
LCST	Lower critical solution temperature
LG	Lauryl gallate
LUMO	Lowest unoccupied molecular orbital
PBLG	Polybenzyl glutamate
PMMA	Polymethyl methacrylate
PNIPAM	Poly(<i>N</i> -isopropylacrylamide)
PVA	Polyvinyl alcohol
REM	Raster electron microscopy
UCST	Upper critical solution temperature
UV	Ultraviolet

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Chromogenic polymers change their visible optical properties in response to an external stimulus. The chromogenic phenomena enable the integration of sensor and actuator functionality or any kind of information into a material.

This Update focuses on thermochromic phenomena in polymers.

Thermochromism can appear in all different classes of polymers: thermoplastics, duroplastics, gels, inks, paints or any type of coatings. The polymer itself, an embedded thermochromic additive or a supermolecular system built by the interaction of the polymer with an incorporated non-thermochromic additive can cause the thermochromic effect.

The content of this review is structured by the thermochromic material type. At the end of each chapter the state-of-the-art of existing as well as potential future applications based on specific material classes is discussed.



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